

Natural Attenuation of Volatile Organic Compounds (VOCs) in the Leachate Plume of a Municipal Landfill: Using Alkylbenzenes as Process Probes

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Abstract

More than 70 individual VOCs were identified in the leachate plume of a closed municipal landfill. Concentrations were low when compared with data published for other landfills, and total VOCs accounted for less than 0.1% of the total dissolved organic carbon. The VOC concentrations in the core of the anoxic leachate plume are variable, but in all cases they were found to be near or below detection limits within 200 m of the landfill. In contrast to the VOCs, the distributions of chloride ion, a conservative tracer, and nonvolatile dissolved organic carbon, indicate little dilution over the same distance. Thus, natural attenuation processes are effectively limiting migration of the VOC plume. The distribution of C₂₋₃-benzenes, paired on the basis of their octanol-water partition coefficients and Henry's law constants, were systematically evaluated to assess the relative importance of volatilization, sorption, and biodegradation as attenuation mechanisms. Based on our data, biodegradation appears to be the process primarily responsible for the observed attenuation of VOCs at this site. We believe that the alkylbenzenes are powerful process probes that can and should be exploited in studies of natural attenuation in contaminated ground water systems.

Introduction

As of 1996 there were 3091 municipal landfills operating in the United States (U.S. Environmental Protection Agency, <http://www.epa.gov/epaoswer/non-hw/munpl/factbook/internet/lanf/ldf.htm#2>, accessed November 2000). The number of closed landfills, many of which are unlined, poorly capped, and sited on alluvial deposits, could be as high as 100,000 (Sufliuta et al. 1992). In these unlined landfills, chemical constituents of the solid wastes and substances produced by the breakdown of the wastes are leached from the landfill by infiltrating water. The leachate is ultimately transported to the water table where it mixes with ambient ground water and is advected away from the deposit forming a contaminant plume. The leachate plume is subject to complex hydrologic and biogeochemical processes that determine the ultimate fate of landfill-derived pollutants. Understanding the interplay of these processes may make it possible to predict and, therefore, limit the

impact of toxic substances entering ground water systems from municipal landfills.

Studies performed to date have shown that a large number of volatile organic compounds (VOCs) are typically found in landfill leachate and leachate plumes (Christensen et al. 1994). The most commonly observed VOCs include the halogenated hydrocarbons and aromatic hydrocarbons such as BTEX (benzene, toluene, ethylbenzene, and the xylenes) and the C₃- to C₅-benzenes. In some cases, extensive plumes several hundreds of meters long have developed downgradient from the source (Reinhard et al. 1984). More commonly, the VOCs are attenuated within a short distance from the landfill (Lyngkilde and Christensen 1992; Rügge et al. 1995). Attenuation can result from a combination of physical, chemical, and biological processes. It is of interest to know which of these processes dominate in a given environment because this may assist in development of effective remedial strategies.

Observed variations in the organic chemical composition of leachate plumes suggest that biodegradation can be an important process in the removal of specific VOCs (Reinhard et al. 1984; Lesage et al. 1990; Rügge et al. 1995). In this context, compounds having the same chemical formula but different structures (i.e., isomers) serve as powerful indicators of natural biodegradation processes. The reason is that isomers have closely similar and sometimes identical physico-chemical properties. Changes in the relative abundance of an isomer pair within a leachate plume can-

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Received September 1999, accepted August 2000.

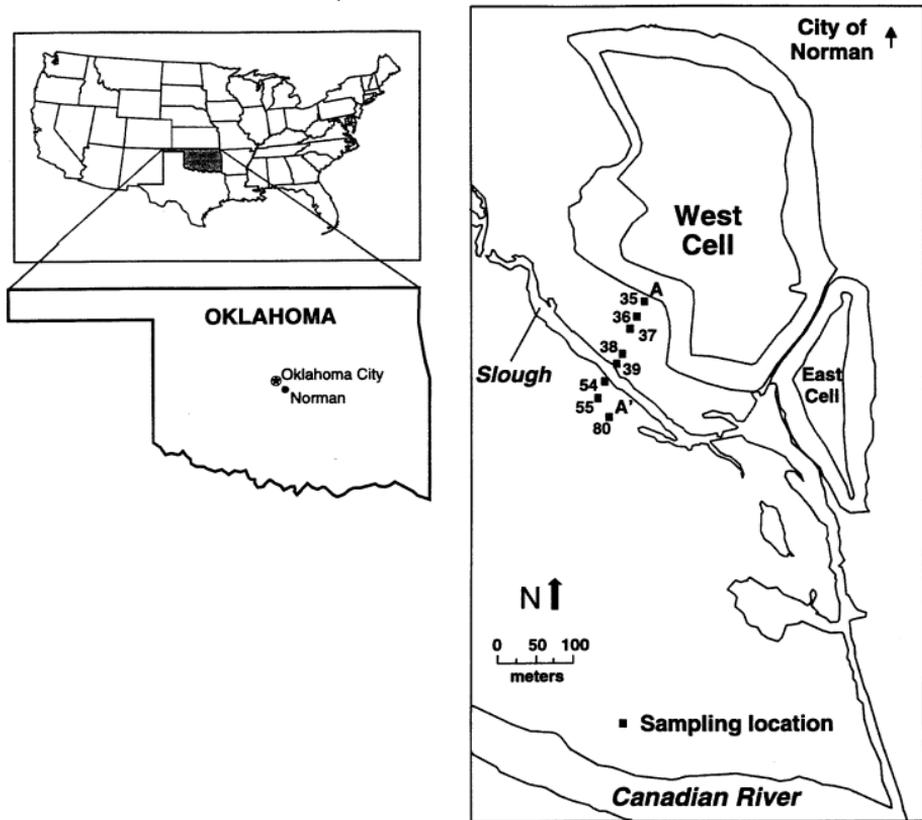


Figure 1. Map of the Norman, Oklahoma, landfill showing locations where ground water samples were collected.

not be attributed to physical-chemical attenuation processes because such processes affect each isomer in the same way (Eganhouse et al. 1993a, 1996; Wiedemeier et al. 1995). Assuming chemical reactions can be excluded from consideration, biodegradation is then left as the dominant process of removal. Interpretations based on changes in chemical composition, even for isomer pairs, can sometimes be complicated by uncertainties in the spatial and temporal variation of VOC inputs from the landfill (Kjeldsen 1993; Kjeldsen et al. 1998a, 1998b; Barker et al. 1986). Laboratory and in situ microcosm experiments conducted in leachate plumes have also shown the potential for biodegradation of various VOCs under a range of redox conditions (Wilson et al. 1986; Nielsen et al. 1995; Bjerg et al. 1999). Frequently, however, it is difficult to correlate the results of microcosm experiments with VOC compositional changes observed in the field (Bjerg et al. 1999; Rügge et al. 1995). In order to better understand and predict the course of natural attenuation,

we need to develop methods that allow identification and quantitation of relevant processes (physical, biological, and chemical) in the field.

This paper describes early studies of the volatile organic compounds in the leachate plume of a municipal landfill. Our objectives were: (1) to identify potential molecular markers of landfill leachate, and (2) to examine processes affecting the natural attenuation of VOCs in leachate plumes. Molecular markers are compounds that come from a specific source and can be used to track the movement of contaminants from that source in the environment (Eganhouse 1997). As distinct from other nonspecific tracers of leachate, such as chloride ion or δD_{H_2O} , molecular markers may or may not behave conservatively. Consequently, they can be useful both for delineating plume geometry and in understanding processes that control the transport and fate of organic contaminants in complex hydrologic environments. In this context, we have used the VOCs as process probes.

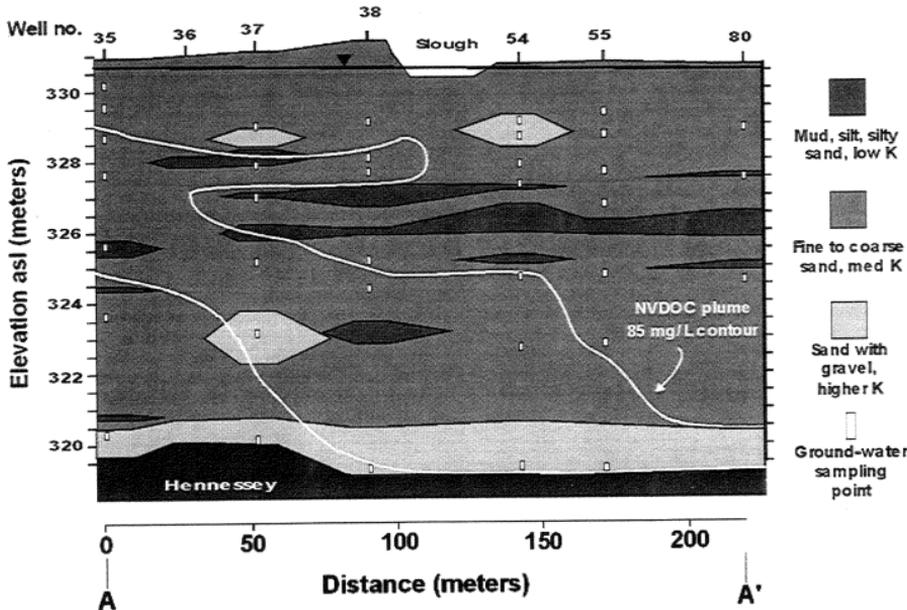


Figure 2. Generalized permeability structure in the alluvial aquifer. Sampling locations and the A-A' sampling transect are shown in Figure 1. Sampling points for DOC plume samples depicted here (Cozzarelli et al. 1999) are not to scale. "K" represents hydraulic conductivity. Vertical exaggeration is = 18:1.

Site Description

The study site is a closed, unlined municipal landfill located near the city of Norman, Oklahoma, adjacent to the Canadian River (Figure 1; Christenson et al. 1999). The present configuration of the landfill consists of two units, an east cell and a west cell. The cells rise to a maximum height of approximately 12 to 13 m. The alluvium upon which the wastes were deposited is 10 to 12 m thick and is underlain by a low permeability unit (the Hennessey Group; Figure 2) composed of shale and mudstone. This serves as a basal confining unit for the surficial aquifer. The alluvium consists primarily of medium-grained sand and silty sand interbedded with mud and gravel. A slough located approximately 50 to 100 m downgradient from the landfill is a surface expression of the local water table that appears to receive some leachate input as well as recharging fresh water (Schlottmann et al. 1999). The slough is a remnant of the former river channel and, thus, runs roughly parallel to the edge of the landfill.

The water table is less than 2 m below land surface in the vicinity of the leachate plume downgradient from the landfill (Figure 2). Hydraulic conductivity, measured by slug tests, is generally 2.4×10^{-7} m/s to 2.8×10^{-4} m/s (Scholl et al. 1999; Christenson et al. 1999), excluding clay layers, which were not measured. Ground water flow near the main leachate plume of the west cell is to the southwest toward the Canadian River (Figure 1). Average ground water velocity in the area between the slough and the landfill is estimated at 28 m/yr, using Darcy's law with the median value of

hydraulic conductivity, a measured porosity of 0.40, and head gradient over the area of interest. Figure 2 presents a conceptual diagram of the permeability structure of the aquifer along a NE-SW transect originating at the west cell (A-A' on Figure 1; after Scholl et al. 1999). Mud-silt layers of low permeability are found at elevations of approximately 325 to 328 m above sea level (asl). A high permeability layer, dominated by coarse sand and gravel, exists at the base of the alluvium (319 to 320 m asl). Superimposed on the generalized permeability structure depicted in Figure 2 is the 85 mg/L isopleth of the nonvolatile dissolved organic carbon (NVDOC) plume (after Cozzarelli et al. 1999). The NVDOC plume is bifurcated by the low permeability mud-silt layer. The shallow branch of the plume may discharge to the slough, whereas the deeper branch extends to the base of the alluvium and is found more than 200 m downgradient within the high permeability layer.

Methods

Sampling

Figure 1 shows locations where ground water was collected for VOC analysis. The sampling locations form a nonlinear NE/SW transect (A-A') that extends approximately 200 m from the down-gradient edge of the landfill in the general direction of ground water flow. Samples were obtained in November 1995 and April 1996 using drive point wells pounded to the desired depth with an electric jackhammer (Cozzarelli et al. 1999). The temporary wells

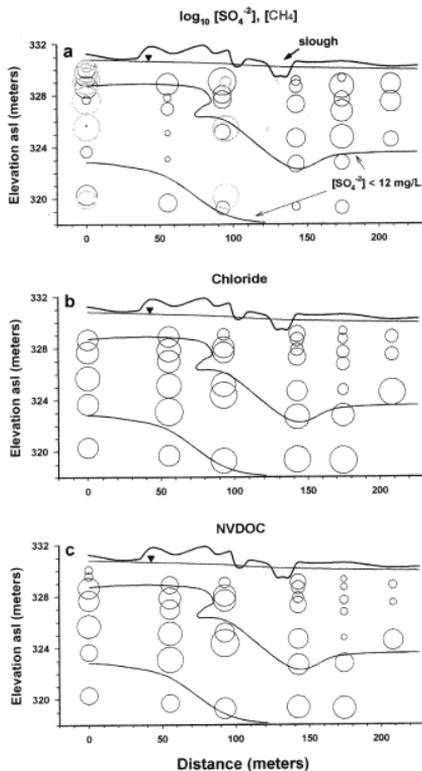


Figure 3. Distribution of (a) sulfate and methane, (b) chloride, and (c) NVDOC in the leachate plume downgradient from the Norman, Oklahoma, landfill. Bubble diameter are proportional to concentration (mg/L). Maximum concentrations: sulfate = 510 mg/L, methane = 10.5 mg/L, chloride = 110 mg/L, NVDOC = 160 mg/L. See Figure 1 for locations of wells.

were made of precleaned Schedule-80 stainless steel pipe connected to stainless steel screened sandpoints, 8.7 cm in length.

Once the drive point had been pounded to the desired depth, ground water was pumped to the surface with a peristaltic pump using Teflon® tubing attached directly to the sandpoint. The well was purged until ground water was free of particles and geochemical conditions (pH, conductivity, temperature) had stabilized. Samples for a variety of inorganic constituents were then collected as described by Cozzarelli et al. (1999). Immediately afterwards, samples for VOC analysis were collected into 40 mL amber VOC vials as detailed by Eganhouse et al. (1993b). The VOC samples were poisoned with HgCl₂, spiked with a recovery surrogate solution containing *o*-xylene-D₁₀, sealed without headspace, and stored on ice. Upon return to the laboratory, VOC samples were kept in a refrigerator until analyses could be performed.

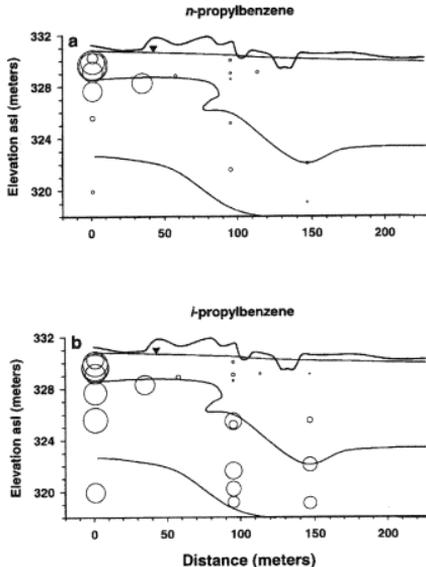


Figure 4. Distribution of (a) *n*-propylbenzene, and (b) *i*-propylbenzene in the alluvial aquifer downgradient from the Norman, Oklahoma, landfill. Concentrations (µg/L) are proportional to bubble diameter. Maximum concentrations: *n*-propylbenzene = 0.80 µg/L, *i*-propylbenzene = 1.24 µg/L. Curved line in saturated zone is the 12 mg/L sulfate isopleth corresponding to the core of the anoxic leachate plume.

Analytical Procedures

The ground water samples were analyzed for VOCs by purge-and-trap capillary gas chromatography with ion trap detection (P&T-CGC/ITD) using methods based on those described by Eganhouse et al. (1993b). The procedure involves determination of benzene, toluene, C₂₋₄-benzenes and naphthalene by the internal standard method using a Tekmar LSC2000 P&T equipped with a Tekmar ALS2016 autosampler. The transfer line from the P&T was directly connected to a fused silica capillary column (30 m × 0.25 mm I.D., 0.25 µm film thickness: DB-5 or DB-5ms; J&W Scientific) by means of a stainless steel zero dead volume union, both maintained in a Varian 3400 high-resolution gas chromatograph. The analytical column was directly interfaced to a Finnigan 800a ion trap detector.

Just prior to analysis, samples were spiked with an internal quantitation standard solution containing ethylbenzene-D₁₀. Additional quality control procedures included the analysis of laboratory blanks, field blanks, and sample duplicates. Method detection limits (MDLs) for 40 analytes ranged from 0.002 to 0.093 µg/L. Average blank concentrations ranged from below detection limits to 0.13 µg/L. The concentrations of analytes in samples were low, falling below the MDL in approximately 35% of the cases. Recoveries of *o*-xylene-D₁₀ in ground water samples were 70 ± 13% (mean ± 1 std dev; n = 42). Analysis of replicate samples indicated that the precision of this method is ≤ 10% (coefficient of variation). Identification of compounds discussed in this paper is based on com-

Table 1
Compounds Identified in the Leachate Plume of the Norman, Oklahoma, Landfill

Hydrocarbons	α -methylstyrene
benzene ^a	3-methylstyrene
toluene ^a	camphene
<i>m</i> -xylene ^a	indan
<i>p</i> -xylene ^{a,b}	C ₁ -indans
<i>o</i> -xylene ^{a,b}	C ₂ -indans
ethylbenzene ^a	C ₃ -indans
<i>i</i> -propylbenzene ^a	teralin
<i>n</i> -propylbenzene	C ₁ -tetralins
1-methyl-2-ethylbenzene	C ₂ -tetralins
1-methyl-3-ethylbenzene	
1-methyl-4-ethylbenzene	Oxygen-Bearing Compounds
1,2,3-trimethylbenzene	fenchone ^{c,d}
1,2,4-trimethylbenzene	benzaldehyde
1,3,5-trimethylbenzene	1,4-cineole ¹
<i>t</i> -butylbenzene ^e	1,8-cineole
<i>iso</i> -butylbenzene	desmethylenfenchone
<i>sec</i> -butylbenzene	campholine epoxide ¹
<i>n</i> -butylbenzene	1-methylpropoxybenzene ¹
1-methyl-2-propylbenzene	1,4-dioxane
1-methyl-3-propylbenzene	acetone ¹
1-methyl-4-propylbenzene ¹	1,3-oxathiolane
1-methyl-2- <i>i</i> -propylbenzene	
1-methyl-3- <i>i</i> -propylbenzene	Chlorinated Hydrocarbons
1-methyl-4- <i>i</i> -propylbenzene	chlorobenzene ^a
1,2-diethylbenzene	1,2-dichlorobenzene ^a
1,3-diethylbenzene	1,4-dichlorobenzene ^a
1,4-diethylbenzene	trichloroethylene
1,2-dimethyl-3-ethylbenzene	chloroform
1,2-dimethyl-4-ethylbenzene	dichloromethane
1,3-dimethyl-2-ethylbenzene	chloromethylbenzene
1,3-dimethyl-4-ethylbenzene	
1,3-dimethyl-5-ethylbenzene ¹	
1,4-dimethyl-2-ethylbenzene	
naphthalene ^a	
2-methylnaphthalene	
1-methylnaphthalene ^a	

^aCompounds also identified by the U.S. EPA (Wilson 2000).

^bCompounds also identified by Dunlap et al. (1976).

¹Tentative identification.

parison of mass spectral data with published mass spectra and/or P&T-CGC/ITD analysis of authentic compounds. Further details concerning the performance of the method are given in Eganhouse et al. (1993b).

The concentration of nonvolatile dissolved organic carbon was determined by the persulfate wet oxidation technique described by Baedecker and Cozzarelli (1992), and chloride ion concentration was determined by ion chromatography using a Dionex Series 4000i ion chromatograph.

Results and Discussion

Composition of VOCs in the Leachate Plume

Table 1 lists some of the more than 70 volatile organic compounds we have identified in the leachate plume samples. We estimate that these represent 85% of the total VOC concentration. Many of these same compounds have been reported in other landfill studies (see references in Christensen et al. 2000), and a few have been observed previously by researchers investigating the Norman landfill leachate plume (Dunlap et al. 1976; Wilson 2000).

The VOCs fall into three groups: (1) hydrocarbons, (2) oxygen-bearing compounds, and (3) chlorinated hydrocarbons. The hydrocarbons are dominated by the monoaromatics (BTX + C₂-C₄-benzenes, and methylstyrenes). Significant but variable amounts of naphthalene, alkylated naphthalenes, and a variety of alicyclic hydrocarbons were also found. The oxygen-bearing compounds are composed mainly of plant-derived natural products such as fenchone, 1,4-cineole, and 1,8-cineole. Several common, presumably anthropogenic, substances or degradation products such as acetone, 1,4-dioxane, and benzaldehyde were found in low abundance. The chlorinated hydrocarbons, most of which probably arise from solvents, are few in number and, with the exception of the chlorobenzenes, occur in low abundance when compared with the other compound classes.

Eganhouse et al. (1999) discuss some of the many possible sources of VOCs we have identified in the leachate plume. The sources that contain the greatest number of these VOCs are: (1) solvents, (2) petroleum/petrochemical products and processes, (3) coal/coke and related materials, (4) chemicals used as feedstock and intermediates in chemical synthesis (synthetic), (5) plant materials, and (6) resins and paints. Whereas multiple sources could exist for most of the VOCs, all of the recognized sources can contribute a mixture of compounds. This finding is consistent with the heterogeneous nature of the wastes likely to have been deposited in the landfill.

Finally, we have identified several compounds that may serve as potential molecular markers of the leachate. These are chlorobenzene, 1,4-dichlorobenzene, *i*-propylbenzene (Figure 4b), *t*-butylbenzene, 1,2,3-trimethylbenzene and 1,4-cineole. All of these VOCs are relatively abundant and are persistent within the core of the anoxic leachate plume downgradient from the landfill. It is important to note, however, that the concentrations of even the most persistent VOCs are reduced to the level of their detection limits within 200 m of the edge of the landfill (see the following). Reinhard et al. (1984) and Barker et al. (1986) found that chlorobenzene and 1,4-dichlorobenzene were persistent in the methanogenic portion of the North Bay landfill leachate plume, and Wilson and Rees (1985) demonstrated that chlorobenzene was highly stable under methanogenic conditions in microcosm studies of the Norman landfill. Our findings are consistent with these observations.

Abundance of VOCs in the Leachate Plume

Table 2 lists concentration ranges for some of the compounds we have determined in the leachate plume samples. Also shown are ranges reported by Christensen et al. (1994, 2000) for the small, but growing, literature on landfill chemistry, data taken from a study by Gibbons et al. (1999), and drinking water standards promulgated by the U.S. EPA. The data of Gibbons et al. (1999) come from measurements of VOCs in leachate of hazardous and municipal waste landfills where the division between "old" and "new" is 1987 and 1985, respectively. By this criterion, the Norman landfill would be categorized as an "old" municipal landfill.

In all cases but one (naphthalene), the concentrations of individual and isomer groups that we observe in the leachate plume of the Norman landfill are in the low $\mu\text{g/L}$ range. Of the compounds listed, only benzene was found at a concentration that exceeded U.S. drinking water standards. The concentrations fall in the lower end and sometimes below the lower end of ranges reported for other landfills by Christensen et al. (2000). This is not entirely surprising because many of the highest concentrations reported in the lit-

Table 2
Comparison of VOC Concentrations ($\mu\text{g/L}$) Found in Norman, Oklahoma, Landfill Leachate Plume, Those Reported in Literature, and U.S. EPA Drinking Water Standards

Compound	Norman Landfill	Reported in Literature ^a	Landfills by Type ^b				Drinking Water Standards ^c
			Hazardous		Municipal		
			Old	New	Old	New	
benzene	0-10	1-1630	440	580	40	23	5
toluene	0-3.5	1-12,300	1500	1400	210	330	1000
Xylenes ^d	0-1	4-3500	—	—	—	—	10,000
ethylbenzene	0-0.1	1-1280	720	360	96	72	700
Σ trimethylbenzenes ^e	0-0.6	4-250	—	—	—	—	—
naphthalene	0-38	0.1-260	—	—	—	—	—
chloroform	0.02-0.04	1-70	—	—	—	—	—
1,1,1-trichloroethane	0.09	0.1-3810	440	—	—	38	200
trichloroethylene	0.6-0.7	0.7-750	720	95	10	19	5
chlorobenzene	—	0.1-110	600	300	31	—	100
1,4-dichlorobenzene	0.1-5.6	0.1-16	—	—	—	—	75

^aAfter Christensen et al. (2000).

^bAfter Gibbons et al. (1999). Concentrations are 95% nonparametric confidence limits for median concentrations.

^cwww.epa.gov/OGWDW/mcl.html (June 2000).

^dXylenes = [*o*-xylene + *p*-xylene + *m*-xylene].

^eTrimethylbenzenes = [1,2,3-trimethylbenzene + 1,2,4-trimethylbenzene + 1,3,5-trimethylbenzene].

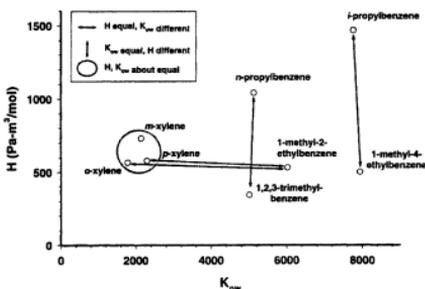


Figure 5. Scatterplot showing the distribution of Henry's law constants (H) and octanol-water partition coefficients (K_{ow}) for $C_{2,3}$ -benzenes used in analysis of natural attenuation processes.

erature are for sites where large quantities of industrial wastes were disposed (Först et al. 1989; Lesage et al. 1990). The solid wastes deposited in the Norman landfill are believed to have been predominantly of residential and commercial origin. The landfill was not permitted to accept hazardous or industrial wastes, and there is only unconfirmed anecdotal mention of an incident of suspected hazardous waste disposal (Dixon 1992). In addition, the literature data reported by Christensen et al. (1994, 2000) include results for samples of leachate as well as ground water contaminated by leachate. Thus, the upper limits in such tabulations are probably not strictly representative of leachate plumes downgradient from landfills. Finally, the literature data may be biased because of analytical limitations. To be specific, it is possible that other published studies have used methods with MDLs that are significantly higher than the one used in this study. If so, some VOCs may have gone undetected and, therefore, unreported by other investigators.

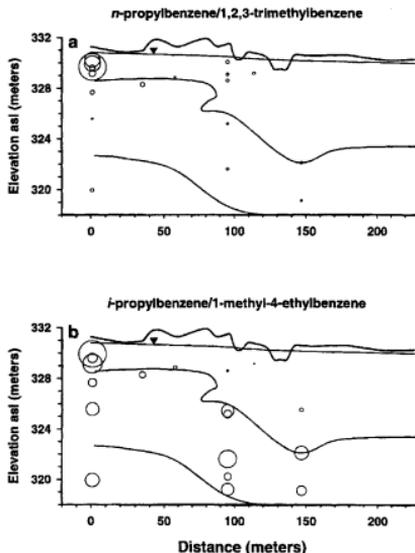


Figure 6. Distribution of concentration ratios for C_3 -benzene isomer pairs having equivalent octanol-water partition coefficients but different Henry's law constants: (a) *n*-propylbenzene/1,2,3-trimethylbenzene; (b) *i*-propylbenzene/1-methyl-4-ethylbenzene. Curved line in saturated zone is the 12 mg/L sulfate isopleth corresponding to the core of the anoxic leachate plume.

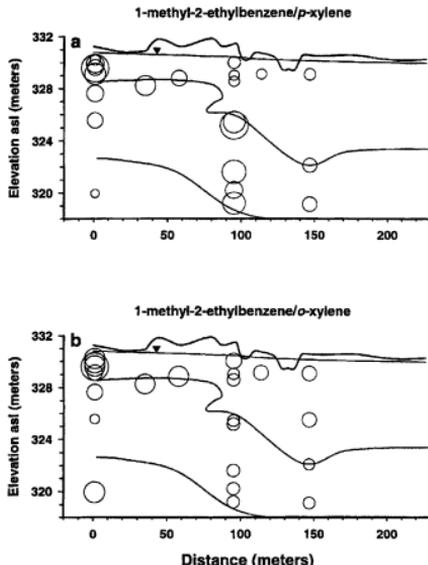


Figure 7. Distribution of concentration ratios for C_{2,3}-benzenes having equivalent Henry's law constants but different octanol-water partition coefficients: (a) 1-methyl-2-ethylbenzene/p-xylene; (b) 1-methyl-2-ethylbenzene/o-xylene. Curved line in saturated zone is the 12 mg/L sulfate isopleth corresponding to the core of the anoxic leachate plume.

The data of Gibbons et al. (1999) help place the present results in context. These authors examined a large number of VOC measurements in leachate samples collected from hazardous, codisposal, and municipal solid waste landfills. Statistical analysis of the data revealed that the chemical composition of leachate from these three landfill types could be readily distinguished and that the VOC concentrations observed for municipal landfills are one to two orders of magnitude lower than those in hazardous waste landfills (Table 2). Thus, the low VOC concentrations we have found in the leachate plume of the Norman landfill are consistent with the current understanding of old municipal landfills.

In order to assess the potential importance of VOCs in carbon cycling, we estimated the proportion of total DOC represented by the total VOCs. For this computation we assumed that the average carbon content of benzene + C₁₋₄-benzenes is 91% and that these compounds make up 25% of the total VOCs. Total DOC concentration was then estimated by adding the DOC concentration of the total VOCs to the measured NVDOC concentration. Based on quantitation of benzene + C₁₋₄-benzenes in the Norman leachate plume samples, our calculations show that the VOCs represent less than 0.1% of the total DOC. Thus, these compounds are not quantitatively important in fueling biogeochemical reactions in the aquifer. Similar findings have previously been reported by Barker et al. (1986) for the municipal landfill in North Bay, Canada.

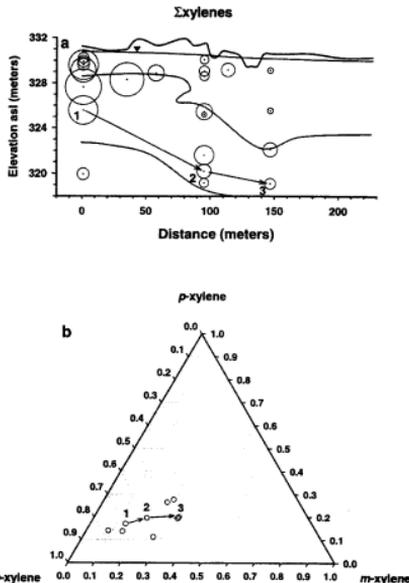


Figure 8. (a) Cross section showing positions at which VOC samples were collected (dots) and bubble plot of total xylylene concentration (concentration \propto bubble diameter). Also shown is the 12 mg/L sulfate isopleth corresponding to the core of the anoxic leachate plume. Arrows connect samples collected along a flowpath (1-2-3) at the approximate center line of the plume. (b) Ternary diagram of the xylylene isomers (normalized to total xylylene concentration). Arrows indicate evolution of xylylene composition for samples collected along the approximate center line of the plume (see panel 8a). Other data points correspond to sampling points within the core of the anoxic plume shown in panel 8a.

Distribution and Fate of VOCs in the Leachate Plume

Figure 3 shows the distribution of sulfate, methane, chloride, and NVDOC in ground water downgradient from the landfill. Because sulfate and methane concentrations vary over more than three orders of magnitude, these data have been log transformed. Cozzarelli et al. (1999) have shown that all of the portion of the aquifer depicted in Figure 3 is anoxic. The dominant terminal electron accepting processes are sulfate reduction and methanogenesis (Cozzarelli et al. 2000; Harris et al. 1999). Lowest sulfate concentrations and highest methane concentrations are found within a highly reducing core of the anoxic leachate plume. As delineated by the 12 mg/L sulfate contour, the core of the anoxic leachate plume is found at greater depth with increasing distance downgradient from the landfill, ultimately reaching the base of the aquifer at a distance of approximately 130 m. The observed pattern results from two phenomena: (1) recharge from rainfall and from the slough enters the aquifer above the plume, diluting and pushing it down, and (2) the presence of the high permeability layer at the base of the aquifer (Figure 2) serves as a conduit.

Chloride, a conservative tracer of the leachate, shows little or no change in concentration within the core of the anoxic plume (Figure 3b), suggesting that dilution due to hydrodynamic dispersion is limited. The distribution of NVDOC (Figure 3c) is similar to that of chloride, with highest concentrations (>150 mg/L) being found within an envelope that descends with increasing distance downgradient from the landfill. The maximum concentrations of NVDOC are approximately 50 to 75 times those found in native ground water (Cozzarelli et al. 1999). Within the core of the anoxic leachate plume, NVDOC concentrations show little or no observable change, indicating that most of the substances making up this portion of the DOC pool are not efficiently remineralized. These patterns are in sharp contrast to the behavior of the majority of the VOCs.

Most, but not all, of the aromatic hydrocarbons exhibit distributions in which their concentration decreases rapidly with increasing distance from the landfill, ultimately falling below detection limits within a distance of 200 m. An example of this type of pattern is shown in Figure 4a where the distribution of *n*-propylbenzene is depicted in a bubble plot. Although we presently do not have data on the temporal variability of the *n*-propylbenzene concentration in source leachate, it is reasonable to assume (given the age of the landfill) that the source term for this compound has not increased over time. Thus, the decreasing concentration with distance from the landfill cannot be explained by an increasing supply of *n*-propylbenzene from leachate. Because chloride and NVDOC concentrations show no significant change within the core of the anoxic plume (Figure 3), *n*-propylbenzene and most of the other VOCs, which exhibit similar patterns, must be attenuated during transport. By contrast, a few VOCs appear to persist within the anoxic plume downgradient from the landfill. An example of this latter type of behavior is shown in Figure 4b, where the distribution of *i*-propylbenzene is plotted. Although the concentration of this compound in the core of the anoxic leachate plume decreases with distance from the landfill, the rate and extent of attenuation is significantly reduced as compared to *n*-propylbenzene.

In the following discussion we examine the use of pairs of alkylbenzenes for elaboration of processes responsible for the observed attenuation. The basis for this analysis is that compounds having identical or closely similar physico-chemical properties should have the same distribution within the core of the anoxic plume unless differences in compound-specific biodegradation rates cause them to differ (Reinhard et al. 1984; Eganhouse et al. 1996; Allen-King et al. 1996). By examining pairs of alkylbenzenes that have systematically different properties, we can evaluate the relative importance of volatilization (Henry's law constant), sorption (octanol-water partition coefficient), and biodegradation. The approach consists of two steps: selection of pairs of compounds having identical or systematically different physico-chemical properties, and examination of their relative distribution in the aquifer using concentration ratios. For this analysis, we assume that the concentrations of these compounds in the leachate have not increased over time.

Of the 36 aromatic hydrocarbons determined in this study, six were not considered for this analysis because of partial coelution or other chromatographic limitations. Eight compounds were eliminated from consideration because in more than 39% of the samples we analyzed, these VOCs were either absent or present at concentrations below the MDL. This left 22 monoaromatic hydrocarbons. Of these, only eight were identified for which appropriate

physico-chemical property data were available. Figure 5 shows octanol-water partition coefficients (K_{ow}) and Henry's law constants (H) for these eight compounds. K_{ow} values determined by Sherblom and Eganhouse (1988) were employed because partition coefficients were determined for all of the compounds of interest using the same reversed-phase high performance liquid chromatographic method. Henry's law constants were obtained from Mackay et al. (1992) who selected data compiled from the literature.

First, we consider the case of compounds having the same tendency for sorption to aquifer solids (as indicated by K_{ow}), but large differences in their tendency to volatilize (as indicated by Henry's law constant). This is illustrated in Figure 6 where the concentration ratios of *n*-propylbenzene/1,2,3-trimethylbenzene and *i*-propylbenzene/1-methyl-4-ethylbenzene are plotted. The K_{ow} values of these isomer pairs are within 2.5% of each other, but the Henry's law constants of the propylbenzenes are roughly three times those of the isomers with which they are paired. In the absence of biodegradation, one would predict that the concentration ratios should decrease as these compounds are transported downgradient from the landfill because volatilization would cause the numerator to decline more rapidly than the denominator. What we observe, however, is that within the core of the anoxic leachate plume (as delineated by the 12 mg/L sulfate contour), there is no systematic change in the ratios. This suggests that in the core of the plume, volatilization is not the dominant process controlling attenuation of these compounds and that sorption and/or biodegradation must be considered. This generalization is valid because the range of Henry's law constants exhibited by these particular isomer pairs spans that of virtually all of the C_{0-4} -benzenes (Mackay et al. 1992). At this field site, where the plume is sinking below the water table, there is little reason to believe that volatilization should be an important process within the core of the anoxic plume. Thus, the trends depicted in Figure 6 are consistent with our expectations.

As a second case, we consider compounds having the same tendency for volatilization but different sorptive behavior. Isomers cannot be employed in this analysis because their K_{ow} values are similar. However, it is well known that the octanol-water partition coefficient increases with alkylation of the benzene ring (Sherblom and Eganhouse 1988; Figure 5). Consequently, we rely here on monoaromatic hydrocarbons having different numbers of carbon atom substituents. Figure 7 illustrates the distribution of the 1-methyl-2-ethylbenzene/*p*-xylene and 1-methyl-2-ethylbenzene/*o*-xylene concentration ratios. The Henry's law constants of these isomer pairs are within 10% of each other, but the K_{ow} value of 1-methyl-2-ethylbenzene is roughly three times greater than that of *o*-xylene and *p*-xylene (Figure 5). Again, the range of K_{ow} values for these compound pairs spans that of most of the C_{2-3} -benzenes (Sherblom and Eganhouse 1988). If sorption was the dominant process causing attenuation of the C_{2-3} -benzenes within the core of the anoxic leachate plume, one would predict that the concentration ratios would decrease as the hydrocarbons were transported downgradient from the landfill. Instead, the ratios appear to increase or, at most, remain constant within the core of the anoxic leachate plume. This strongly suggests that sorption to aquifer solids is not the dominant process controlling the attenuation of the C_{2-3} -benzenes in this zone.

One could reasonably argue that by process of elimination, biodegradation must be the dominant process controlling attenuation of these VOCs in the anoxic leachate plume. This hypothesis can be examined directly by comparing the behavior of isomers hav-

ing identical physico-chemical properties. Among the compounds considered here, the ones that come nearest to satisfying this requirement are the xylene isomers (Figure 5). [The xylene isomers have Henry's law constants and K_{ow} values that range from 565 to 730 Pa·m³/mol (Mackay et al. 1992) and 1780 to 2290 (Sherblom and Eganhouse 1988), respectively.] One way to examine the compositional variation of these isomers within the core of the anoxic leachate plume is through the use of a ternary diagram. Lipson and Siegel (2000) recently demonstrated how ternary diagrams could be used effectively to identify the most important processes controlling the fate of benzene, toluene, and the xylenes (BTX). Here we are interested in evaluating whether compositional variations in the xylene isomers exist in the leachate plume, and if so, what these variations might reveal about the fate of these VOCs.

In the absence of biodegradation and assuming the composition of the leachate has remained the same over lifetime of the plume, the relative abundance of the xylene isomers should be constant within the aquifer. However, examination of the data plotted on the ternary diagram (Figure 8b) reveals that xylene composition within the core of the anoxic leachate plume is variable. Some of this variation might be attributed to the small differences in hydrophobicity (K_{ow}) and volatility (H) of the xylenes. However, comparison of C_{2,3}-benzenes having nearly identical Henry's law constants but widely different K_{ow} values (Figures 5 and 7) showed no observable effect on their relative abundance. Thus, we do not believe the much smaller differences in K_{ow} among the xylene isomers can account for the compositional variation seen in Figure 8b.

Although it is not presently possible to accurately define a flowpath in this system, we assume that samples within the core of the anoxic leachate plume nearer the landfill had been resident in the plume for a shorter period at the time of collection than those further downgradient. Under these circumstances, one would expect to find a consistent relationship between xylene composition and distance from the landfill. Figure 8a indicates the locations of the wells sampled in this study in relation to the core of the anoxic plume (dots). Also shown are data (bubbles) for the total xylene (i.e., *o*-xylene + *m*-xylene + *p*-xylene) concentration at these sampling points. Three samples, taken from the approximate center line of the plume (1-2-3; connected by arrows) are believed to represent a possible flowpath. This assertion is based on the closely similar chloride (836 to 1020 mg/L) and NVDOC concentrations (101 to 123 mg/L) of these particular samples. Along this flowpath total xylene concentration is seen to decrease. This occurs because the concentrations of all three xylene isomers also decrease over the same distance (*o*-xylene: 0.45→0.04 µg/L; *m*-xylene: 0.08→0.03 µg/L; *p*-xylene: 0.11→0.02 µg/L).

Changes in the xylene isomer composition of these samples are shown in Figure 8b. Assuming the samples are representative of ground water along a flowpath, there appears to be a progressive enrichment in *p*-xylene and *m*-xylene (at the expense of *o*-xylene) as the anoxic plume moves through the aquifer. The change in composition reflects different rates of attenuation as indicated by the more rapidly decreasing concentration of *o*-xylene as compared with *m*- and *p*-xylenes. Because sorption and volatilization do not exert a dominant control on removal of C_{2,3}-benzenes from the anoxic plume (as shown by the preceding analysis), this trend must reflect differences in the rates of biodegradation of the xylene isomers. Although the physico-chemical properties of the xylenes are similar (Figure 5), *o*-xylene has the lowest Henry's law constant and octanol-water partition coefficient of the three isomers. Thus,

if physical-chemical processes were controlling changes in xylene isomer composition, one would expect the concentration of *o*-xylene to be attenuated least. What we observe is exactly the opposite. This clearly identifies biodegradation as the cause for the observed changes in xylene composition.

It is difficult to explain the xylene compositions of the other samples taken from the core of the anoxic plume because they do not follow the trajectory of the three samples taken from the approximate center line. There are at least three possible explanations for this apparent discrepancy. First, many of the former samples are found on the periphery of the plume where conditions may be variable with respect to redox conditions and dominant electron accepting processes. Second, the samples may not represent a flowpath and, thus, may not be comparable. Alternatively, temporal variations in leachate composition may have been greater than we are assuming for this analysis. More extensive sampling of the leachate plume and long-term temporal sampling, both ongoing at this time, should provide further insights to this question.

Conclusions

Leachate from the Norman landfill has contaminated the surficial alluvial aquifer. The spatial distribution of the VOCs in the leachate plume downgradient from the landfill is determined by a combination of hydrologic and biogeochemical factors. Based on observations to date, the most important of the hydrologic factors appear to be recharge to the shallow aquifer and physical heterogeneity of the aquifer (Christenson et al. 1999; Scholl et al. 1999). Our preliminary results indicate that the monoaromatic hydrocarbons are the most abundant class of VOCs at this site. The sources of the VOCs are diverse, reflecting the wide range of anthropogenic and natural materials that have historically been employed in the landfill. Concentrations of the VOCs appear to be in the low µg/L range and are among the lowest that have been reported in the literature. This is probably due to the age of the landfill and the fact that it was not used for disposal of large quantities of industrial solvents and other chemicals. It may also be a reflection of the low method detection limits we achieved with the ion trap detector.

Concentrations of most of the VOCs decrease rapidly within a short distance downgradient from the landfill. All are near or below detection limits within 200 m. The fact that chloride and NVDOC concentrations remain essentially constant over the same distance suggests that the downgradient extent of the VOC plume is limited by attenuation processes. The question is, "Which processes dominate?" By measuring a wider range of monoaromatic hydrocarbons than is usually determined in ground water monitoring studies, we were able to select compound pairs having similar or identical physico-chemical properties for further study. These compounds were then used as process probes to systematically evaluate the relative importance of volatilization, sorption and biodegradation. Because monoaromatic hydrocarbons are among the most commonly observed pollutants in contaminated ground water systems, this approach should have widespread applicability.

Technical protocols for demonstrating natural attenuation typically rely on several lines of evidence (e.g., ASTM 1998; Wiedemeier et al. 1995). These include documentation of the loss of contaminants of concern, evidence based on various geochemical indicators, and ancillary evidence such as solute transport modeling and/or microbiological studies. Developing the data necessary to demonstrate natural attenuation is costly and time con-

suring. In this study we used selected C_{2-3} -benzenes to demonstrate that biodegradation was the most important process affecting the fate of VOCs at this site. We believe this approach is a valuable ancillary tool that can be particularly useful for characterizing natural attenuation when extensive temporal and spatial monitoring data are not available.

Acknowledgments

The authors wish to thank the following individuals for their assistance in sample collection and installation of wells: Scott Christenson, Dale Ferree, Jim Pontolillo, John Roach, and Jamie Schlottmann. We greatly appreciate the efforts of Tyler Coplen and Rama Kotra who reviewed an early draft of this paper. We also appreciate the valuable suggestions provided by Richelle M. Allen-King, Walton Kelly, and an anonymous reviewer. This research was made possible by support from the U.S. Geological Survey Toxic Substances Hydrology Research Program.

Editor's Note: The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the National Ground Water Association.

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